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{Enter Vessel Company Name}

# Quality Assurance/Quality Control Plan For Sampling and Analysis of Treated Sewage and Graywater From Commercial Passenger Vessels Prepared by ADEC CPVEC Program January 15, 2004

Submitted to fulfill certain requirements of Alaska Statute 46.03.460 – 46.03.490 and 18 AAC 69

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1 Toject ivianagei	Signature	Date
Sampling Manager <sup>1</sup>		
	Signature	Date
Lab Manager		
	Signature	Date
Denise Koch, ADEC Project Manager		
	Signature	Date
Ron Klein ADEC Water Quality Moni (Acting QA Officer)	toring and Assessment Pro	gram Manager
	Signature	Date
The document control form	at will consist of the follow	ving:
Revision Number Revision Date:		
the Quality Assurance/Qual	lity Control Plan (QA/QCP	upper right corner of each page of b). Each revision of the QA/QCP (1 (one) to the previous revision

Small Ship Wastewater Monitoring # Quality Assurance/ Quality Control

Plan

On the bottom of each page will be found:

 $<sup>^{1}</sup>$  This person could be the sampler or the person who supervises the sampler.

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### **Distribution List**

A copy via electronic format of each revision will be distributed to the following individuals:

<u>Individual</u> <u>Organization</u>

Denise Koch ADEC Project Manager

Ron Klein ADEC Water Quality Monitoring &

Assessment Program Manager

(Acting QA Officer)

Lab Manager To be named
Sample Manager To be named
Vessel Representatives To be determined

### Acronyms/Abbreviations Used

ADEC Alaska Department of Environmental Conservation

BNA Base/Neutrals, Acids

BOD Biochemical Oxygen Demand – 5-day test

CFR Code of Federal Regulations

COC Chain of Custody

COD Chemical Oxygen Demand DOO Data Quality Objective

EPA Environmental Protection Agency

HDPE High Density Polyethylene

HCl Hydrochloric Acid H<sub>2</sub>SO<sub>4</sub> Sulfuric Acid HNO<sub>3</sub> Nitric Acid

MDL Method Detection Limit
MSD Marine Sanitation Device
NaOH Sodium Hydroxide
%R Percent Recovery

PQL Practical Quantitation Limit (Minimum Reporting

Level)

QA Quality Assurance

QA/QCP Quality Assurance/Quality Control Plan

QMP Quality Management Plan

QC Quality Control

RPD Relative Percent Difference

RQ Reportable Quantity per 40 CFR part 302

SM Standard Methods SW-846 Solid Waste Methods

SOP Standard Operating Procedures

TSS Total Suspended Solids
VOCs Volatile Organic Chemicals
VSSP Vessel Specific Sampling Plan

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### **Management and Contractors**

### **Vessel Representatives/Project Managers**

Individual representatives of small cruise ship companies or the Alaska Marine Highway System (AMHS) may elect to follow this generic QA/QCP in order to satisfy obligations under Alaska Statute 46.03.465(b) and 18 AAC 69.025. (*The QA/QCP that a vessel operator chooses to follow will be indicated in the vessel's registration document.*)

This representative oversees the sampling and lab contract. This person is responsible for compliance with this QA/QCP. Responsibilities include:

- Ensuring coordination among vessels crew, samplers, lab, and ADEC.
- Communicating project information to the sampler, lab, and ADEC
- Assuring that project participants have necessary training.
- Fielding questions and requests for information that arises during and after the project.
- Managing the financial aspect of the project.
- Attaching field notes to sample results, chain of custody and providing the ADEC with any deviations to the QA/QC Plan or VSSP.

### **Sampling Manager and Team**

The QAQC plan must be signed by all parties before sampling begins. The VSSP must be approved by the ADEC prior to sampling.

All sampling will be coordinated and conducted by the Sample Manager and sampling team whose credentials must be approved by ADEC 21 days prior to sampling<sup>2</sup>.

The sampling manager will design a tentative sampling schedule. The sampling manager must submit the schedule to the ADEC with the VSSP. The sampling manager or their designee will notify the ADEC a minimum of 36 hours prior to the sampling. This notice gives ADEC the opportunity to audit the ship's sampling procedures.

Sampling Manager will be responsible for sample collection, sample integrity and custody, field measurements, and accurate notes. A compilation of field notes, deviations from VSSP or QA/QCP plans (if applicable), and Chain of Custody will be provided to the laboratory personnel and vessel representative and the Project Quality Assurance Officer upon completion of all sampling.

### Lab Manager and Wastewater Analysis Laboratory

A laboratory, certified for drinking water analysis by ADEC, will be retained to analyze both conventional and priority pollutant samples according to their individual laboratory Quality Assurance Plan, and using EPA-approved analytical methods. A list of ADEC certified Microbiological Labs is available at <a href="http://info.dec.state.ak.us/eh/dwww/labs.htm">http://info.dec.state.ak.us/eh/dwww/labs.htm</a> and labs that provide chemical analysis is available at

http://info.dec.state.ak.us/eh/lab/certchemlabs.aspx The Lab Manager is responsible that

<sup>&</sup>lt;sup>2</sup> 18 AAC 69.090 lists what ADEC uses to determine whether a person is qualified to sample.

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laboratory data information is verified and validated before it leaves the laboratory. The Lab Manager signs off verified and validated laboratory information.

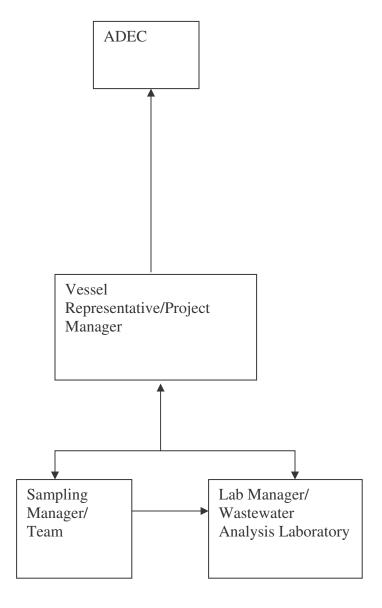
### **ADEC Project Manager**

The ADEC Project Manager is responsible for managing the program to meet the requirements in the Alaska Statute, regulation and the approved QA/QC plan.

### **ADEC Water Quality Assurance Officer**

The ADEC Water Quality Assurance Officer will review the QA/QCP to determine if it meets the State of Alaska's objectives for the data collection effort. The ADEC WQA Officer may review data results and participate in sampling and laboratory audits.

## **2004 Program Organizational Chart**



### **Purpose**

This document is prepared and submitted to fulfill requirements of Alaska Statute 46.03.460- 46.03.490, and 18 AAC 69.025. The state law requires at least two **sampling events** per vessel in a season. A "sampling event" is the collection of representative samples of each wastewater type being discharged within Alaska waters. The number of samples in a sampling event is based on the ship configuration, vessel wastewater management practices, and the wastewater quantities discharged while the sample team is on-board. The samples must be taken at a point in the system directly before being discharged overboard as determined by the approved VSSP. The samples must be taken while the vessel is discharging into ambient water.

### **Applicability**

This QA/QCP specifies the minimum requirements for sampling and analysis of treated sewage and/or graywater and other wastewaters as defined in AS 46.03.490 discharging into the applicable waters of Alaska as defined in 33 CFR 159.305 and the waters of the Alexander Archipelago as defined in AS 46.03.490. All sampling events required by AS 46.03 shall be conducted in accordance with this QA/QCP. Owner/operator must provide documentation verifying their compliance with the guidelines in AS 46.03.460-46.03.490, and 18 AAC 69, 18 AAC 70 and this plan.

Each participating ship must be sampled within 45 days of initial entry into Alaska waters and be subject to DEC sampling audits. The ADEC may perform additional sampling and analysis inspections as necessary to implement AS 46.03.

This QA/QCP covers sampling and analysis for the parameters listed below. Analysis for conventional pollutant parameters required by ADEC under AS 46.403.465 and is noted by an asterisk (\*). The ADEC will also require analysis of priority pollutant parameters under AS 46.403.465. A sample that fails to provide valid results for all required pollutants as indicated by an asterisk will not be counted as an acceptable sample for purposes of meeting the minimum requirement of two samplings for conventional pollutants.

**Conventional pollutants (two sampling events):** 

	<u>'</u>
Total Suspended Solids (TSS)*	Settleable Solids (SS)
Biochemical Oxygen Demand (BOD)*	Oil and Grease
Chemical Oxygen Demand (COD)*	Total Organic Carbon
Ammonia – Total*	Specific Conductance (to measure seawater influx)
Fecal Coliform*	Alkalinity
pH*	Total Nitrogen (Ammonia, Nitrate, Nitrite, and Total
	Kjeldahl Nitrogen (TKN))
Total and Free Residual Chlorine*	Total Phosphorus

<sup>&</sup>lt;sup>3</sup> The VSSP for each vessel will list the proper location and timing of wastewater sampling. The samples will be taken in a manner that seeks to capture a typical wastewater discharge while still meeting the fecal coliform 6-hour holding time.

### **Priority Pollutants (one sampling event)**

- Base/Neutrals, Acids
- Volatile Organic Chemicals (VOCs)
- Trace Metals (Total Recoverable and Dissolved)
- Cyanide

### **Blind Duplicate Samples**

Blind sample duplicates must be collected on a minimum of 10% of the total number yearly samples for the company or one sample, whichever number is greater. The blind samples will be analyzed for conventional pollutants and trace metals.

The purpose of the blind sample duplicates is to assess sampling and laboratory error and to assess overall method variability. The use of duplicate samples extends the test of precision to the sampling method itself. The use of blind samples provides a test of the laboratory and is used to assess bias or analytical errors not detected by the laboratory (e.g., a false positive). The samples will be analyzed by the same lab and for the same parameters. The sampler must obtain and deposit a large quantity of sample into a 10 liter sterile cube. The sample will then be mixed and poured into the individual preserved sample bottles provided by the lab for the duplicate sample.

### Quality Objectives and Criteria for Measurement Data

Data Quality Objectives (DQOs) are quantitative and qualitative objectives that define usable data for meeting the requirements of this project. DQOs define the quality of services provided by the laboratory and are used in the quality assurance review of the field and laboratory data. Review of the quality control (QC) data against the DQOs determines if the data are fully usable, considered estimates, or rejected as unusable.

### **Quantitative DQOs**

The quantitative DQOs for this project include reporting limits, precision, accuracy, and completeness.

### Reporting Limits.

Reporting limits are determined by laboratory-provided or method-specified minimum levels, or by interim minimum levels where reporting limits at or near water quality criteria are not obtainable. Individual analyte reporting limits are listed in Table 2.

### Precision.

Precision is the ability to replicate the measurement. It is expressed as Relative Percent Difference (RPD). Acceptance criteria for RPD are analysis-specific and are defined by

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the laboratories. RPD is normally determined by matrix spike duplicates or by laboratory-fortified blank duplicates. The calculation for RPD is:

$$((X_1 - X_2) / ((X_1 + X_2)/2))*100,$$

and is expressed as a percent.  $X_1$  = first sample measurement and  $X_2$  = second sample measurement. Precision limits for specific analytes are listed in table 4.

### Accuracy.

Accuracy is the closeness of the measurement to the true level of the variable. Accuracy is expressed as percent recovery (%R). Acceptance criteria for %R vary depending on the method. %R is normally determined by the use of known traceable laboratory control standards. Acceptance limits for accuracy for each analyte are listed in Table 2.

### Completeness.

Completeness is a measure of how many planned measurements for each constituent actually resulted in usable data. It is expressed as a percentage of the total number of samples collected. The completeness criterion for this project is 80 percent. Because of the variety of vessels and discharges sampled, and the possibility for weather or other shipping-related delays resulting in missed holding times, a completeness criterion of less than 100% is to be expected.

### **Qualitative DQOs**

The qualitative DQOs are representativeness and comparability.

### Representativeness.

Representativeness is a measure of how well the sample reflects the typical wastewater effluent. The vessel owner and operator will define sample representativeness in the vessel specific sampling plans (VSSP). VSSPs are developed by each vessel participating in the program in consultation with the Vessel Representative. A representative sample is the effluent of a continuous treatment system or the discharge port as a holding tank (or tanks) containing a majority of the wastewater produced in a day. The VSSP is designed to ensure that consistent sampling methods are followed and that samples are collected from appropriate and representative locations at appropriate times.

### Comparability.

Comparability is a measure of confidence with which one data set can be compared to another. It is addressed in the plan by 1) following USEPA standardized sampling and analytical methods; 2) by using similar sampling and analytical methods as followed in last year's monitoring project; 3) ensuring that appropriate reporting limits are used; and 4) obtaining data of known and acceptable quality through the use of specified QC measures and QA data assessment.

Because of the different source types found on different vessels (e.g., a holding tank on some ships may contain both blackwater and graywater, while on others it may only contain graywater), careful definition of discharge types will be made in the VSSP. It is

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essential that these definitions be carried through to the end data user, as these differences could erroneously bias data interpretation. The sampler must obtain the vessel's speed and position in longitude/latitude at the tine of sampling. Information added to the VSSP or changes to the VSSP during the sampling event must be recorded on the VSSP, COC, or in the field notes and must accompany the samples to the lab and be provided to the project data recipients as part of the complete report.

### Special Training Requirements/Certification

Samplers will be trained in sampling methods, sample handling, chain of custody, and field measurements as outlined in 40 CFR 136. Additionally, samplers will receive appropriate training through their employer or their employer's designee, in any necessary shipboard safety procedures.

Laboratories used will have a current Alaska Department of Environmental Conservation Drinking Water certification. Laboratory analysts will be trained in accordance with each laboratory's QA Plan and Standard Operating Procedures (SOPs). Records of current certification, analyst training, and the laboratory QA documents listed above will be made available to the Vessel representative, the Project QA Officer, and ADEC upon request. Laboratories will employ approved methods of testing as outlined in 40 CFR 136.

### **Documentation and Records**

### Sample schedule and Vessel/Sample Identification

The sampler must include a tentative schedule in the Vessel Specific Sampling Plan. The sampler must also notify the ADEC of its intent to sample at least 36 hours prior to sample collection. The two sampling events must be a minimum 21 days apart unless being conducted as a "re-sampling" allowed under 18 AAC 69.070.

Samples will be identified clearly on the chain of custody and sample bottles. For example, a sample from the Laundry Graywater from the *M/V Hypothetica* will be identified as "Laundry Graywater," as the description with associated dates and times. The Sample ID should clearly state where the sample was taken. For example, a mixed black and gray sample taken from the MSD discharge line is MSD BW as its sample ID. Holding tanks should be HT. Collection tanks should be labeled CT. All samplers should use the same sample ID system.

### Field Records

The sampler will write Field notes on a bound field notebooks with numbered pages or on a checklist. On-board staff initial the field notes. Included in the field notes for each sample are:

- Vessel name (e.g., *Hypothetica*),
- Sampling personnel,
- Shipboard assistants,
- Photos and description of sample ports,
- Sample date and times,
- Field measurements: pH, chlorine residual, and temperature,

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- Records on discharge flow rates and holding tank volumes,
- Samples collected,
- Nature of sample: Composite or Grab,
- Waste type: blackwater, graywater, or mixed,
- Deviations from VSSP and/or OA/OCP,
- Unusual conditions and explanation of data anomalies,
- Latitude/longitude and speed at time of discharge being sampled,
- Copy of the Discharge record for the sampled discharge.

### Laboratory Records

Upon completion of laboratory analysis, laboratory data review, and data validation, the laboratory will issue a full report in an electronic format describing the results of analysis for each sample submitted. Prior to issuance of the analytical report to the vessel's representatives, the laboratory's QA manager will review and approve the report. The laboratory will scan the copied materials from the sampler and include them in the electronic format.

### Components of the analytical report include:

- A short summary sheet discussing the sampling event and results.
- Sample information: ship name, sample names, waste type, date and time collected.
- Parameter name and method reference.
- Analytical result.
- Method Detection Limit.
- Practical Quantitation Limit (reporting limit).
- Date and time of sample preparation and date and time of analysis.
- Quality control information: blank results, spiked blank or laboratory control standard recovery, matrix spike/spike duplicate recoveries, relative percent differences between duplicate spike analyses.
- Chain of custody.
- Holding times met or not.
- Case Narrative of deviations from methods, procedural problems with sample analysis, holding time exceedances, and any additional information that is necessary for describing the sample. This narrative should explain when results are outside the precision and accuracy required and the corrective actions taken to rectify these OC problems.
- Discharge logs and field notes.
- Deviations from VSSP or QAQC Plan
- Latitude and longitude information pertaining to each sample including which overboard port the waste was discharged through and the speed the vessel was traveling.
- Explanation of data abnormalities.
- If applicable, a notification that this sample is a resample under 18 AAC 69.070
- Copy of the Chain of Custody

### Chain of Custody

The original chain of custody form will accompany the sample to the laboratory. When portions of the sample are sent to another laboratory (e.g., for many of the priority pollutants), a copy of

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the chain of custody will be made and this will accompany the samples. At each transfer of the sample, the transfer will be indicated on the chain of custody form. The person listed on the Chain of Custody should have full sight or control of the sample at all times until it the COC is relinquished by that person and received by the next party signed on the COC.

A copy of the original chain of custody will be included with the final report.

### Sampling Process Design

A vessel specific sampling plan (VSSP) will be developed for each ship by the ship engineers and submitted to the sampling team 21 days prior to sampling. This plan needs to be approved by the ADEC. The plan will include elements listed in 18 AAC 69.030, and as a minimum, the following:

- Vessel name.
- Passenger and crew capacity of ship.
- Daily water use per individual.
- Locations and capacities for treated sewage, graywater, and other wastewater tanks.
- Type of wastewater treatment systems.
- Each discharge pump type and rate
- Vessel schematic of discharge ports and corresponding sampling ports.
- Description of discharges, including anticipated flow rates and tank volumes.
- Table containing type of discharge, type of sample (grab or composite), parameters (conventional or priority pollutants), location on the vessel where each sample is to be collected, and special circumstances.
- A narrative description of the time at which each sample is to be taken based upon circumstances that will yield a sample most likely to be representative of the average discharge that passes through the location where the sample is taken
- A description of the standards the owner or operator will use to determine a deviation from the plan
- Equipment required.

Each VSSP will be dated and a copy will be provided to the ADEC. The ADEC must approve the VSSP prior to sampling. After the first sampling event on a vessel, the VSSP may be updated. If it is updated, copies of the updated sampling plan and approved by the ADEC before the second round of sampling occurs.

### Sample Collection Procedures

Specific sampling techniques for each vessel will be detailed in the VSSP. The following general guidelines are listed to provide consistency among the vessels utilizing this QA/QCP.

Samples will reflect a representative discharge of treated blackwater, graywater and other wastewaters into applicable waters of Alaska from an operable marine sanitation device, other treatment system, a holding tank or some combination as specified in the VSSP. Samples may be taken only from water that the vessel is discharging to ambient water. If samples must be taken while the ship is underway, care will be taken to assure sample representativeness and homogeneity.

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A volume of water equal to at least ten times the volume of the sample discharge line will first be discharged into a bucket or similar container to clear the line of standing water and possible contamination.

Samplers will wear disposable gloves, tyvek suit and safety eyewear and will observe precautions while collecting samples, remaining aware of the potential biohazard present.

Samplers will take care not to touch the insides of bottles or lids/caps during sampling.

Samples will be listed as "grab" on the Chain of Custody form.

Bottles will be pre-cleaned and will not require rinsing with sample. When sample bottles are pre-preserved, bottles must never be rinsed but will be filled only once with sample.

Samples will be cooled immediately in an ice-water bath to  $4^{\circ}$  C and then placed into a cooler containing frozen blue ice or ice and water mixture to maintain a sample temperature of  $4 + /-2^{\circ}$  C. Temperature will be measured and recorded at the time of sample collection and a note shall be made of the temperature of the cooler contents upon arrival at the laboratory.

Sample bottles will be filled sequentially. Bottles will normally be filled to the shoulder of the bottle, leaving a small space for expansion and mixing. VOC bottles will be filled leaving a convex meniscus at the top of the bottle, with no air bubbles present; when the VOC lid is screwed on a small volume of water will be displaced and no air will be present in the bottle. Filtering of dissolved metals will be performed immediately upon receipt at the laboratory followed by preservation through acidification.

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Table 1. Sample Containers, Preservations, Holding Times, Sample Types

LAB	CONTAINER	PRESERVATION	HOLDING TIME	Grab or	Sample
PARAMETER	CONTAINER	IKESEKVATION	HOLDING TIME	Composite	Timing/
				_	Collection
Conventional Pollu	ıtants				
Total Suspended	From BOD	4° C	7 days	Grab	Dependent
Solids	bottle		J	Only	upon
Settleable Solids	1 liter	4° C	48 hours	Grab	vessel (see
	HDPE, white label			Only	individual vessel
Biochemical	1 liter	4° C	48 hours	Grab	sampling
Oxygen Demand	HDPE, white			Only	plan)
78	label				1 /
Ammonia – Total	250 ml	H <sub>2</sub> SO <sub>4</sub> , pH <2, 4° C	28 days	Grab	
	HDPE,	Lab pre-preserved	·	Only	
	yellow label				
Chemical Oxygen	From	H <sub>2</sub> SO <sub>4</sub> , pH <2, 4° C	28 days	Grab	
Demand	ammonia	Lab pre-preserved		Only	
	bottle				
Specific	From BOD	4° C	28 days	Grab	
Conductance	bottle			Only	
Fecal Coliforms	100 ml	Sodium Thiosulfate, 4°	6 hours	Grab	
	sterile plastic	С		Only	
Alkalinity	From BOD	4° C	14 days	Grab	
	bottle			Only	
pН	100 ml	4° C	ASAP	Grab	
	HDPE and		In field and lab	Only	
	from BOD				
0.1 1.0	bottle	11.00 11.0.40.0	20.1	G 1	
Oil and Grease	1 liter glass	$H_2SO_4$ , pH <2, 4° C	28 days	Grab	
	2.10	Lab pre-preserved	• • •	Only	
Total Organic	2 40-ml	$H_2SO_4$ , pH <2, 4° C	28 days	Grab	
Carbon	VOC vials	Lab pre-preserved	• • •	Only	
Total Nitrogen	500 ml	$H_2SO_4$ , pH <2, 4° C	28 days	Grab	
	HDPE,	Lab pre-preserved		Only	
	yellow label				
Total Phosphorus	From	$H_2SO_4$ , pH <2, 4° C	28 days	Grab	
	ammonia	Lab pre-preserved		Only	
	bottle				
Temperature	From pH	N/A	ASAP in field	Grab	
	Bottle			Only	
Chlorine Residual	From pH	N/A	ASAP	Grab	
	bottle		In field	Only	

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<b>Priority Pollutants</b>					
BNA	1 liter glass	4° C; Sodium	7 days until	Grab	Dependent
		Thiosulfate if residual	extraction	Only	upon
		chlorine is present.			vessel (see
VOCs	3 40-ml	HCl, 4° C; Sodium	14 days until	Grab	individual
	VOC vials	Thiosulfate if residual	analysis	Only	vessel
		chlorine is present			sampling
					plan)
Total Recoverable	500 ml	$HNO_3$ , $pH < 2$ ,	28 days Hg/ 6 mos.	Grab	
Metals	HDPE	4° C	Others	Only	
Dissolved Metals	500 ml	Filtration w/0.45	6 months	Grab	
	HDPE	micron filter, HNO <sub>3</sub> ,		Only	
		pH <2			

Sample containers will normally be pre-preserved by the laboratory. If chlorine residual is detected during field measurement of chlorine, sodium thiosulfate provided by the lab will be added in the field to the BNA until no chlorine is detected. The lab must provide decanting bottles with sodium thiosulfate. When chlorine is detected, the sample will be added first to the decanting bottle, and then will be decanted into the VOC vials.

### Sample Handling and Custody Requirements

### Sample Custody

Samples and sample containers will be maintained in a secure environment, from the time the bottles leave the laboratory until the time the samples are received at the laboratory. The laboratories will maintain custody of bottles and samples using their normal custody procedures.

Blind field duplicates will be identified with discrete sampling labels and recorded as blind field duplicates in the sampler's field notebook.

To maintain the secure environment for samples on board ship and during transport, samples must be: 1) in the sampler's possession (line of sight); or 2) in a cooler sealed with signed and dated friable evidence tape on opposing sides of the cooler; or 3) in a locked cooler for which only the sampler has the key. When the cooler is sealed, the method of securing the samples must be such that tampering with samples or bottles is not possible: The cooler must be secured so that the lid cannot be removed without breaking the evidence tape or cutting the lock, so that tampering would be evident.

Transfer of samples will be accomplished using the laboratory's chain of custody form. When samples are transferred between personnel, such transfer will be indicated on the chain of custody form with signature, date and time of transfer. The chain of custody will remain with the samples, sealed inside the cooler, until received by the laboratory.

At any time during sample transfer, if custody is broken, a note must be made on the chain of custody form accompanying the sample. Upon receipt at the laboratory, the laboratory sample

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custodian will make note if a breach of custody has occurred (for example, if a custody seal has broken during transport).

### Sample Temperature and Condition

Samples will be held at  $4 + /-2^{\circ}$  C. A 1 liter temperature blank will accompany all samples and will be measured at the laboratory upon receipt of the samples to verify the temperature. The temperature of this blank will be recorded on the chain of custody upon receipt of the sample at the lab.

To maintain the temperature, extra blue ice will be kept frozen on board ship or ship ice will be used. Blue ice or ship ice will be exchanged just before shipment of samples to the lab, and may be exchanged more frequently during the sampling trip, as required.

Some samples may be at a temperature near body temperature ( $37^{\circ}$  C) at time of sample collection. This temperature encourages growth of fecal coliform bacteria and thus these samples must be cooled as quickly as possible, without freezing them. These samples shall be placed in a water bath containing ice cubes provided on board ship. The bottles should be immersed in the water to the shoulder, rotated frequently, and ice should be added/water drained off as the ice melts for at least one hour until the sample reaches a temperature of  $4^{\circ}$  C. To ensure custody of these samples that may not be able to be sealed in the cooler until the temperature is lowered, these bottles can be sealed with custody tape individually, as necessary.

In no event will samples be placed in refrigerators meant for human food or beverages.

### Sample Holding Times

Sample holding times are as described in Table 1 above. Planned sample shipping schedules will allow for the meeting of these holding times.

The most critical holding time will be that of fecal coliforms, which is defined by EPA as 6 hours. To meet this holding time, a stringent scheduling effort will be required by the laboratory and samplers. If the normal discharge pattern is altered in order to adhere to this holding time, a note will be made of the change in the field notes and in the final quality control review.

### Sample Disposal

The laboratory must hold samples collected for analysis for at least three months after the sample collection date or as directed by ADEC.

# **Analytical Methods and Quality Control Requirements**

The ADEC requires conventional and priority pollutants reports within 21 days of completion of laboratory analysis.

The MDL referred to in Table 2 below is a statistically derived method detection limit, typically arrived at by repeat analyses performed by the laboratory, with a statistical EPA-defined calculation then performed (40 CFR 136 Appendix B). It is sometimes method-defined (as in, BOD). The PQL (Practical Quantitation Limit) is the level at which the laboratory QA department feels comfortable reporting data. Because the MDL is statistically derived, data can

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be detected at and near the MDL that are not accurate and that are frequently false positives. For this reason, many labs do not report at the MDL but report at some level, often approximately 3 times greater than the MDL (again, for statistical purposes). The MDL and PQL values in this document reflect typical laboratory performance at the present time. Current guidelines for MDL's, RL's (minimum levels, PQL), and precision and accuracy requirements for the project are as follows:

Table 2. ANALYTICAL METHODS AND QUALITY CONTROL REQUIREMENTS

LAB PARAMETER	METHOD*	MDL (mg/l)	Reporting Level Minimum Level	PRECISION (RPD)	ACCURACY (%
			(mg/l)		Recovery)
<b>Conventional Pollutants</b>			. 0		
Ammonia – Total	350.3	0.03	0.10	<20%	85 - 115 %
Biochemical Oxygen Demand	405.1	2	2	<20%	80 - 120 %
Chemical Oxygen Demand	410.1	3	10	<20%	85 - 115 %
Chlorine Residual (total/free)	SM 4500 Cl-G	0.10	0.10	N/A	N/A
Alkalinity	SM 2320 B	0.5	2.0	<20%	85 - 115 %
pH	150.1	0.1 standard units	0.1 standard units	<20%	N/A
Settleable Solids	160.5	0.1 (ml/L)	0.1 (ml/L)	<20%	N/A
Total Suspended Solids	160.2	1.3	4	<20%	85 - 115 %
Fecal Coliforms	SM 9221E	2 FC/100 ml	2 FC/100 ml	N/A	N/A
Specific Conductance	120.1	1 μmHos/cm	2 μmHos/cm	<20%	85 - 115 %
Total Organic Carbon	SM 5310 B	1.0	1.0	<20%	85 - 115 %
Oil and Grease	1664	1.5	5.0	<20%	66-144%
Total Nitrogen	EPA various	1.0	1.0	N/A	N/A
Total Phosphorus	EPA 365.2	0.01	0.05	<20%	85 - 115 %
Priority Pollutants					
Total Recoverable Metals		μg/l	μg/l		
Antimony	200.8	0.15	0.5	<20%	80 - 120 %
Arsenic	200.8	0.15	0.5	<20%	80 - 120 %
Beryllium	200.8	0.15	0.5	<20%	80 - 120 %
Cadmium	200.8	0.15	0.5	<20%	80 - 120 %
Chromium	200.8	0.15	0.5	<20%	80 - 120 %
Copper	200.8	0.15	0.5	<20%	80 - 120 %
Lead	200.8	0.15	0.5	<20%	80 - 120 %
Mercury (Total)	245.1	0.15	0.5	<20%	80 - 120 %
Nickel	200.8	0.15	0.5	<20%	80 - 120 %

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LAB PARAMETER	METHOD*	MDL (ug/l)	Reporting Level		ACCURACY
			Minimum Level	(RPD)	(%
			(mg/l)		Recovery)
Selenium	200.8	0.15	0.5	<20%	80 - 120 %
Silver	200.8	0.15	0.5	<20%	80 - 120 %
Thallium	200.8	0.15	0.5	<20%	80 - 120 %
Zinc	200.8	0.15	0.5	<20%	80 - 120 %
Dissolved Metals					
Antimony	200.8	0.15	0.5	<20%	80 - 120 %
Arsenic	200.8	0.15	0.5	<20%	80 - 120 %
Beryllium	200.8	0.15	0.5	<20%	80 - 120 %
Cadmium	200.8	0.15	0.5	<20%	80 - 120 %
Chromium	200.8	0.15	0.5	<20%	80 - 120 %
Copper	200.8	0.15	0.5	<20%	80 - 120 %
Lead	200.8	0.15	0.5	<20%	80 - 120 %
Nickel	200.8	0.15	0.5	<20%	80 - 120 %
Selenium	200.8	0.15	0.5	<20%	80 - 120 %
Silver	200.8	0.15	0.5	<20%	80 - 120 %
Thallium	200.8	0.15	0.5	<20%	80 - 120 %
Zinc	200.8	0.15	0.5	<20%	80 - 120 %
VOCs					
Acrolein	624	20	100	<20%	50-120%
Acrylonitrile	624	2	10	<20%	60-140%
Benzene	624	0.5	2	<20%	80-120%
Carbon Tetrachloride	624	0.5	2	<20%	80-120%
Chlorobenzene	624	0.5	2	<20%	80-120%
1,2-Dichloroethane	624	0.5	2	<20%	80-120%
1,1,1-Trichloroethane	624	0.5	2	<20%	80-120%
1,1-Dichloroethane	624	0.5	2	<20%	80-120%
1,1,2-Trichloroethane	624	0.5	2	<20%	80-120%
1,1,2,2-Tetrachloroethane	624	0.5	2	<20%	80-120%
Chloroethane	624	0.5	5	<20%	62-133%
Chloroform	624	0.5	2	<20%	80-120%
1,1-Dichloroethene	624	0.5	2	<20%	74-140%
Trans 1,2-Dichloroethene	624	0.5	2	<20%	80-120%
1,2-Dichloropropane	624	0.5	2	<20%	80-120%
1,1-Dichloropropene	624	0.5	2	<20%	80-120%
Ethylbenzene	624	0.5	2	<20%	80-120%
Methylene Chloride	624	1.0	5	<20%	60-140%
Chloromethane	624	1.0	5	<20%	60-140%
Bromomethane	624	1.0	5	<20%	51-131%

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LAB PARAMETER	METHOD*	MDL (ug/l)	Reporting Level	PRECISION (RPD)	ACCURACY
			Minimum Level	(RPD)	(%
		0.7	(mg/l)	200	Recovery)
Bromoform	624	0.5	2	<20%	80-120%
Bromodichloromethane	624	0.5	2	<20%	80-120%
Dibromochloromethane	624	0.5	2	<20%	80-120%
Tetrachloroethene	624	0.5	2 2	<20%	80-120%
Toluene	624	0.5	l .	<20%	80-120%
Trichloroethene	624	0.5	2	<20%	80-120%
Vinyl Chloride	624	0.5	2	<20%	60-140%
2-Chloroethyl Vinyl Ether	624	2.0	10	<20%	60-140%
BNA					
Acenaphthene	625	1.0	5	<40%	48-121%
Benzidine	625	50	200	<40%	30-170%
1,2,4-Trichlorobenzene	625	1.0	5	<40%	40-104%
Hexachlorobenzene	625	1.0	5	<40%	57-142%
Hexachloroethane	625	1.0	5	<40%	60-140%
Bis (2-chloroethyl) ether	625	1.0	5	<40%	38-124%
2-Chloronapthalene	625	2.0	10	<40%	30-170%
1,2-Dichlorobenzene	625	1.0	5	<40%	32-120%
1,3-Dichlorobenzene	625	1.0	5	<40%	60-140%
1,4-Dichlorobenzene	625	1.0	5	<40%	25-92%
3,3'-Dichlorobenzidine	625	5.0	20	<40%	30-170%
2,4-Dinitrotoluene	625	1.0	5	<40%	51-132%
2,6-Dinitrotoluene	625	1.0	5	<40%	34-146%
1,2-Diphenylhydrazine	625	1.0	5	<40%	60-140%
Fluoranthene	625	1.0	5	<40%	51-140%
4-Chlorophenyl Phenyl	625	1.0	5	<40%	53-143%
ether	(25	1.0	~	.4007	52 120 <i>0</i>
4-Bromophenyl Phenyl ether	625	1.0	5	<40%	53-138%
Bis (2-Chloroisopropyl) ether	625	1.0	5	<40%	60-140%
Bis (2-Chloroethoxy) methane	625	1.0	5	<40%	48-122%
Hexachlorobutadiene	625	1.0	5	<40%	60-140%
Hexachlorocyclopentadie	625	2.0	10	<40%	30-170%
ne					
Isophorone	625	1.0	5	<40%	46-118%
Napthalene	625	2.0	10	<40%	45-136%
Nitrobenzene	625	1.0	5	<40%	46-114%
N-Nitrosodimethylamine	625	1.0	5	<40%	30-170%

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LAB PARAMETER	<b>METHOD*</b>	MDL (ug/l)	Reporting Level	PRECISION	ACCURACY
			Minimum Level	(RPD)	(%
			(mg/l)		Recovery)
N-Nitrosodi-N-	625	1.0	5	<40%	39-130%
Propylamine					
N-Nitrosodiphenylamine	625	2.0	10	<40%	60-140%
Bis (2-Ethylhexyl)	625	1.0	5	<40%	56-125%
Phthalate					
Butyl Benzyl Phthalate	625	1.0	5	<40%	55-123%
Di-N-Butyl Phthalate	625	1.0	5	<40%	60-160%
Di-N-Octyl Phthalate	625	1.0	5	<40%	60-140%
Diethyl Phthalate	625	1.0	5	<40%	57-131%
Dimethyl Phthalate	625	1.0	5	<40%	61-123%
Benzo (A) Anthracene	625	1.0	5	<40%	58-118%
Benzo (A) Pyrene	625	1.0	5	<40%	40-138%
Benzo (B) Fluoranthene	625	1.0	5	<40%	41-133%
Benzo (K) Fluoranthene	625	1.0	5	<40%	60-160%
Chrysene	625	1.0	5	<40%	55-139%
Acenaphthylene	625	1.0	5	<40%	48-133%
Anthracene	625	1.0	5	<40%	59-131%
Benzo (g,h,i) Perylene	625	1.0	5	<40%	50-125%
Fluorene	625	1.0	5	<40%	58-130%
Phenanthrene	625	1.0	5	<40%	54-140%
Dibenzo (a,h) Anthracene	625	1.0	5	<40%	50-129%
Indeno (1,2,3-CD) Pyrene	625	1.0	5	<40%	48-125%
Pyrene	625	1.0	5	<40%	46-135%
2,4,6-Trichlorophenol	625	1.0	5	<40%	56-129%
4-chloro-3-methylphenol	625	1.0	5	<40%	49-117%
2-Chlorophenol	625	1.0	5	<40%	38-124%
2,4-Dichlorophenol	625	1.0	5	<40%	55-130%
2,4-Dimethylphenol	625	5.0	25	<40%	58-128%
2-Nitrophenol	625	1.0	5	<40%	52-111%
4-Nitrophenol	625	25	100	<40%	14-122%
2,4-Dinitrophenol	625	25	100	<40%	53-109%
4,6-Dinitro-2-	625	5.0	25	<40%	43-128%
methylphenol					
Pentachlorophenol	625	1.0	5	<40%	37-112%
Phenol	625	1.0	5	<40%	60-140%
*EDA d 1 : IDA d 1 C CI					

<sup>\*</sup>EPA methods in "Methods for Chemical Analysis of Water and Wastes," Environmental Protection Agency, Environmental Monitoring Systems Laboratory - Cincinnati (EMSL-CI), EPA-600/4-79-020, Revised March 1983 and 1979 where applicable. http://www.epa.gov/cgi-bin/claritgw?op-Display&document=clserv:ORD:0167;&rank=4&template=epa

<sup>\*</sup>SM methods in "Standard Methods for the Analysis of Water and Wastewater," 18th or more recent Edition, APHA/AWWA/WEF.

<sup>\*</sup>Four digit numeric methods are from EPA Test Methods for Evaluating Solid Wastes. Physical/Chemical Methods (SW-846). 3<sup>rd</sup> Edition Update 2B, January 1995.

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# Instrument/Equipment Testing, Inspection, and Maintenance Requirements; Calibration and Frequency

Field instruments include a pH test kit, chlorine residual color wheel test kit, and a thermometer.

Maintenance of the chlorine residual test kit includes keeping the sample cell rinsed after sample measurement, keeping the cell clean and free of fingerprints and oils, and keeping the color wheel itself clean. An extra cell will be kept with the test kit in case of breakage or scratches to the sample cell. The field kit should be checked against the lab kit twice per season. Show the calibration of these instruments in field books.

The analysis of pH in the field will be used for reference purposes only and will be verified through laboratory analysis. A pH kit shall be used that ensures the most accurate reading possible in the expected range of pH values. The laboratory will supply reference buffers to the sampling team for field verification.

Laboratory instrument and calibration procedures are detailed in the QA Plans and SOPs from the certified laboratories. Copies of these plans are available upon request from the lab managers or from the Project QA Officer.

### Inspection/Acceptance Requirements for Supplies and Consumables

Sample bottles will be visually inspected prior to sampling. If problems with bottles are noted, such as a cap that has fallen off an empty bottle, note of the problem will be made on the chain of custody form.

Spare parts will be available for all equipment used and Standard Reference Materials and test kit reagents used in sampling will be checked to ensure that they are within expiration dates.

### Inspection/Acceptance Requirements (Non-Direct Measurements)

Historical data for this project includes only three years of monitoring, so data acceptance criteria will not be required for historical data acceptance.

On-board ship data to be recorded includes tank volume and pumping rate data from ship tracking systems and any documented occurrence of seawater influx. The data will be recorded as reported by shipboard staff.

### **Data Management**

Data Management includes accurate field notebook entries, completed Chain-of-Custody forms and laboratory data management documents. Laboratory data management procedures and processes are described in the Laboratory's Quality Management Plan. This document must be available upon request.

The Vessel Representative will report data directly to the ADEC Project Manager after thorough review by the laboratory QA Manager within the regulatory time limits.

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### ASSESSMENT/OVERSIGHT

### **Assessments and Response Actions**

### Field Assessments

ADEC will perform a field sampling audit on randomly chosen sampling events during the season in order to evaluate the performance of the samplers. Follow-up field audits may be necessary pending audit findings. Each audit will concentrate on sampling technique, sample handling, field records, field testing methods, and adherence to vessel specific sampling plans and the QA/QCP. ADEC will send these audit reports to the responsible vessel operator within 14 days of the audit. These reports will include corrective actions, if necessary.

### Laboratory Assessments

Laboratories are subject to periodic and extensive audits by regulatory agency personnel as part of their certification. Reports of these audits will be made available to the ADEC Project Manager and ADEC Water Quality Assurance Officer. The ADEC project manager may review any recent and pertinent technical systems audit reports of the analytical laboratories involved in this project.

### **Duplicates**

Blind sample duplicates will be collected on a minimum of 10% of the total number of annual samples represented by the same vessel representative or one sample per season, whichever number is greater. Companies may take blind duplicates on 10% of the samples taken by their fleet in order to reduce costs. The same lab must be used in this case. Duplicates will be analyzed for conventional pollutants and metals. The purpose of the blind sample duplicates is to assess sampling and laboratory error and to assess overall method variability. Precision between the sample and its duplicate will be determined by calculating the relative percent difference between the two samples, in the same way that precision is measured between two laboratory-fortified blanks or a matrix spike/matrix spike duplicate. The use of duplicate samples extends the test of precision to the sampling method itself. The use of blind samples provides a test of the laboratory and is used to assess bias or analytical errors not detected by the laboratory (e.g., a false positive). The samples will be analyzed by the same lab for the same parameters. Results of the duplicate analysis will be monitored by the Vessel Representative and ADEC Project Manager.

The ADEC QA Officer may conduct a laboratory performance audit.

The ADEC may submit a sample that contains a known concentration of analytes prepared and certified by a different laboratory. The ADEC will compare the results from the lab from the certified sample results to determine the laboratory performance.

The ADEC may submit two trip blank samples over the course of the sampling season. The trip blanks check to see if any outside contamination occurs during the sampling and analyzing process.

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### **Corrective Action**

The laboratory or sampling manager will notify the ADEC Project Manager and Vessel Representative, if errors are noted by the laboratory or sampling personnel. The responsible party will then immediately correct the problem and will send those corrections via email to the Vessel Representative and ADEC Project Manager.

### Reports

The Vessel Representative will issue reports in accordance with the following guidelines:

- All sample results and backup information.
- Blind duplicate samples—Draft report findings to ADEC Project Manager within one week of receiving/verifying results.

The ADEC Project Manager will submit the results of the any QA/QC field sampling audit reports to the Vessel Representative.

### DATA VALIDATION AND USABILITY

### Data Review, Verification, and Validation

During the overall small ship sampling project, the ADEC Project Manager or their designee will review field notes and laboratory data packages to detect correctable problems for the remainder of the study.

Upon receipt of these completed data packages from the Vessel Representative the ADEC Project Manager or designee will review data and field notes to verify that this QA/QCP was followed. Items reviewed will include:

- Comparison of dated vessel specific sampling plans with the QA/QCP to assure that the correct samples were taken.
- Comparison of dated sampling plans with field notes and custody forms to assure that planned samples were collected.
- Review of field notes and data to assure that information specified in the QA/QCP has been recorded.
- Review of laboratory data packets, particularly the QA/QC laboratory sheets.

Any problems noted must be immediately brought to the attention of the Vessel Representative who will notify the Lab Manager or sampler who will take appropriate corrective action as necessary.

### **Reconciliation with Data Quality Objectives**

The ADEC QA Officer or ADEC Project Manager will reconcile the data from this project with the requirements defined in this document following the validation and verification methods stated above. If an overall assessment of these elements cannot ensure that the data are of sufficient quality to meet objectives, then additional evaluation of raw data will be performed.

### **BIBLIOGRAPHY**

Documents referenced during the preparation of this document include:

- 1. April 13 Alaska Cruise Ship Initiative Wastewater Work Group Protocol for Voluntary Wastewater Monitoring Program in 2001.
- 2. July 27, 2000 Cruise Ship Wastewater Monitoring Southeast Alaska 2000 Quality Assurance Project Plan
- 3. EPA Requirements for QA Project Plans (QA/R-5), EPA/240/B-01/003 March 2001.
- 4. US Code of Federal Regulations; including 33 CFR 159.
- 5. Water Quality Standards Handbook, Second Edition, EPA-823-B-94-005a, August 1994.
- 6. Compilation of the U.S. Environmental Protection Agency's Water Quality Criteria for the Priority Toxic Pollutants, ADEC, September 1997.